

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number  
**WO 01/12540 A1**

(51) International Patent Classification<sup>7</sup>: C01B 3/38

(21) International Application Number: PCT/US00/22421

(22) International Filing Date: 15 August 2000 (15.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/375,615 17 August 1999 (17.08.1999) US

(71) Applicant: **BATTELLE MEMORIAL INSTITUTE**  
[US/US]: Pacific Northwest Division, Intellectual Property  
Services, P.O. Box 999, Richland, WA 99352 (US).

(74) Agent: **MAY, Stephen, R.**: Battelle Memorial Institute,  
Pacific Northwest Division, Intellectual Property Services,  
P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

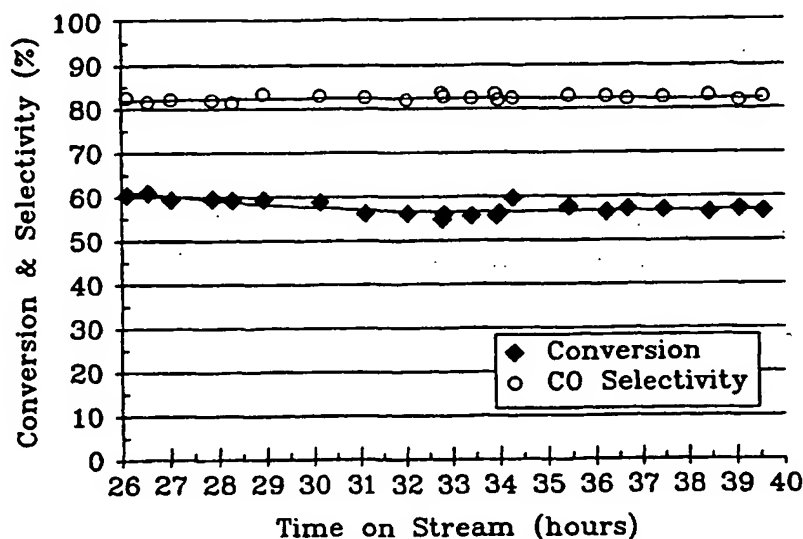
**Published:**

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventors: **WANG, Yong**: 2884 Troon Ct., Richland, WA  
99352 (US). **VANDERWIEL, David, P.**: 2550 Duportail  
St., G-241, Richland, WA 99352 (US). **TONKOVICH,**  
**Anna, Lee, Y.**: 1604 North 37th Place North, Pasco, WA  
99301 (US).

(54) Title: A METHOD AND CATALYST STRUCTURE FOR STEAM REFORMING OF A HYDROCARBON



(57) Abstract: The present invention includes an improvement to the existing method of steam reforming of hydrocarbon, wherein the improvement comprises: the flowing is at a rate providing a residence time less than about 0.1 sec resulting in obtaining product formation yield or amount that is the same or greater compared to product formation at a longer residence time. Another improvement of the present invention is operation at a steam to carbon ratio that is substantially stoichiometric and maintaining activity of the supported catalyst. The present invention also includes a catalyst structure for steam reforming of a hydrocarbon.

WO 01/12540 A1

## A METHOD AND CATALYST STRUCTURE FOR STEAM REFORMING OF A HYDROCARBON

### FIELD OF THE INVENTION

The present invention is a method and catalyst structure for steam reforming of a hydrocarbon.

### BACKGROUND OF THE INVENTION

Steam reforming of hydrocarbons is commonly used for feedstock production for carbon-monoxide hydrogenation (Fischer-Tropsch synthesis), methanol synthesis and hydrogen production. Steam reforming is done commercially by flowing a mixture of steam and the hydrocarbon past a supported catalyst having an alumina support and a catalyst metal thereon, and reacting the mixture at a temperature from about 600 °C to about 1000 °C, forming at least one product. Research has been done with the catalyst metal on a spinel support. Residence times are typically on the order of seconds and steam to carbon ratio greater than about 2.5. For steam to carbon ratio less than 2.5, catalyst activity is generally degraded after hours to days due to coke formation and the supported catalyst must be refreshed or replaced.

The rate of supported catalyst activity degradation has been reduced by use of excess steam (steam to carbon ratio greater than 2.5). Excess steam, however, requires excess thermal energy and results in large system pressure drop. Using less steam results in faster degradation of catalyst activity because of coking from the hydrocarbon(s).

Hence, there is a need for a method of steam reforming of a hydrocarbon that provides greater product yield and permits using less steam and maintaining catalytic activity of the catalyst.

## SUMMARY OF THE INVENTION

The present invention includes an improvement to the existing method of steam reforming of hydrocarbon, wherein the improvement comprises:

the flowing is at a rate providing a residence time less than about 0.1 sec  
5 resulting in obtaining product formation yield or amount that is the same or greater compared to product formation at a longer residence time.

Another improvement of the present invention is operation at a steam to carbon ratio that is substantially stoichiometric and maintaining activity of the supported catalyst.

10 The present invention also includes a catalyst structure for steam reforming of a hydrocarbon. The catalyst structure has

(a) a first porous structure with a first pore surface area and a first pore size of at least about 0.1  $\mu\text{m}$ ;

(b) a porous interfacial layer that is a spinel with a second pore  
15 surface area and a second pore size less than the first pore size, the porous interfacial layer having a thickness less than 4 mm placed upon the first pore surface area;

(c) a steam reforming catalyst selected from the group consisting of rhodium, iridium, nickel, palladium, platinum, carbide of group VIb  
20 and combinations thereof placed upon the second pore surface area.

It is an object of the present invention to provide a method of steam reforming of hydrogen with a residence time of less than about 0.1 sec.

It is an object of the present invention to provide a catalyst structure with a porous interfacial layer of spinel.

25 The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference  
30 characters refer to like elements.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of conversion and selectivity versus temperature.

FIG. 2 is a graph of conversion and selectivity versus time.

5

## DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The present invention includes a method for steam reforming of a hydrocarbon having the steps of flowing a mixture of steam and the hydrocarbon past a supported catalyst having a support and a catalyst metal thereon. The mixture is reacted at a temperature from about 600 °C to about 1000 °C forming at least one product. The improvement of the present invention is using a spinel support and flowing the mixture at a rate providing a residence time less than about 0.1 sec and obtaining product formation that is the same or greater than that obtained at longer residence times.

Also, under the previously described conditions, catalytic activity is degraded when the steam to carbon ratio is substantially stoichiometric. Another improvement of the present invention realized by flowing the mixture at a rate providing a residence time less than about 0.1 sec is maintaining activity of the spinel supported catalyst beyond 6 hours without degradation by coking even for substantially stoichiometric steam to carbon ratio. Substantially stoichiometric is a steam to carbon content ratio greater than about 0.9 and less than about 2.5, preferably from about 0.98 to about 2.

The supported catalyst may be in the form of a powder of non-porous particles, porous solid and combinations thereof.

Hydrocarbon includes oxygenates, alkanes, alkenes, alkynes, branched isomers, aromatics, saturated and unsaturated hydrocarbons and combinations thereof including fuels such as gasoline, kerosine, diesel, JP-8.

30 Example 1

An experiment was conducted to demonstrate the present invention. The supported catalyst was spinel of a gamma-alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) support with a magnesia (MgO) passivation layer and rhodium oxide ( $\text{Rh}_2\text{O}_3$ ). The approximate

composition was about 15 wt%  $\text{Rh}_2\text{O}_3$ , about 5 wt%  $\text{MgO}$ , and about 80 wt%  $\gamma\text{-Al}_2\text{O}_3$ . The supported catalyst was prepared by (1) calcining a high surface area  $\gamma\text{-Al}_2\text{O}_3$  at 500 °C for 5 hours; (2) impregnating the  $\gamma\text{-Al}_2\text{O}_3$  with  $\text{MgO}$  using the incipient wetness technique with a solution of magnesium nitrate; and obtaining  
5 an  $\text{MgO}$  modified  $\gamma\text{-Al}_2\text{O}_3$  support; (3) drying the modified support at 110 °C for 4 hours followed by (4) a second calcination at 900 °C for 2 hours; (5) impregnating the modified support with  $\text{Rh}_2\text{O}_3$  with the incipient wetness technique from a rhodium nitrate solution; (6) followed by a final drying 110 °C for 4 hours and a (7) a final calcination at 500 °C for 3 hours to obtain a powder  
10 of the supported catalyst.

A microreactor was constructed of a quartz tube with 4mm ID and 6.35 mm OD. About 0.2 g of powder of supported catalyst was placed in the microreactor in a packed bed arrangement.

Reactants were steam and methane in a steam to carbon ratio of  
15 approximately 1 which is stoichiometric within measurement uncertainty. Reactants were flowed through the reactor at temperatures from 650 °C to 900 °C.

Results are shown in FIG. 1 for a steam to carbon ratio of 3 with conversion ranging from about 52% to 95% with increasing temperature and  
20 selectivity ranging from 22% to 70%.

Results in FIG. 2 are for a steam to carbon ratio of 1 at 900 °C over 40 hours. No degradation of the supported catalyst was observed. Electron microscopic examination after testing revealed no coke deposition and BET measurements detected no significant loss in surface area.  
25

## CLOSURE

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes  
30 and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

## CLAIMS

We claim:

5

1. A method for steam reforming of a hydrocarbon having the steps of flowing a mixture of steam and said hydrocarbon past a supported catalyst having a support and a catalyst metal thereon, and reacting said mixture at a temperature from about 600 °C to about 1000 °C forming at least one product;  
10 wherein the improvement comprises:

said support is a spinel support; and

said flowing is at a rate providing a residence time less than about 0.1 sec and obtaining said forming the same or greater compared to said forming at a longer residence time.

15

2. The method as recited in claim 1, wherein said mixture has a steam to carbon ratio less than 2.5, said improvement maintaining activity of said supported catalyst beyond 6 hours.

20

3. The method as recited in claim 1, wherein said spinel support controls acidity of said supported catalyst.

25

4. A method for steam reforming of a hydrocarbon having the steps of flowing a mixture of steam and said hydrocarbon having a steam to carbon ratio that is substantially stoichiometric past a supported catalyst having a support and a catalyst metal thereon, and reacting said mixture at a temperature from about 600 °C to about 1000 °C forming at least one product and degrading catalytic activity of said supported catalyst; wherein the improvement comprises:

said support is a spinel support; and

30

said flowing is at a rate providing a residence time less than about 0.1 sec and maintaining activity of said supported catalyst for said steam to carbon ratio less than 2.5.

5. The method as recited in claim 4, wherein said support is spinel that controls acidity of said supported catalyst.

5 6. The method as recited in claim 4, wherein said steam to carbon ratio is greater than about 0.9 and less than about 2.5.

7. The method as recited in claim 4, wherein said supported catalyst is on a porous substrate.

10

8. A catalyst structure for steam reforming of a hydrocarbon, comprising:

(a) a first porous structure with a first pore surface area and a first pore size of at least about 0.1  $\mu\text{m}$ ;

15

(b) a buffer layer upon said first pore surface area;

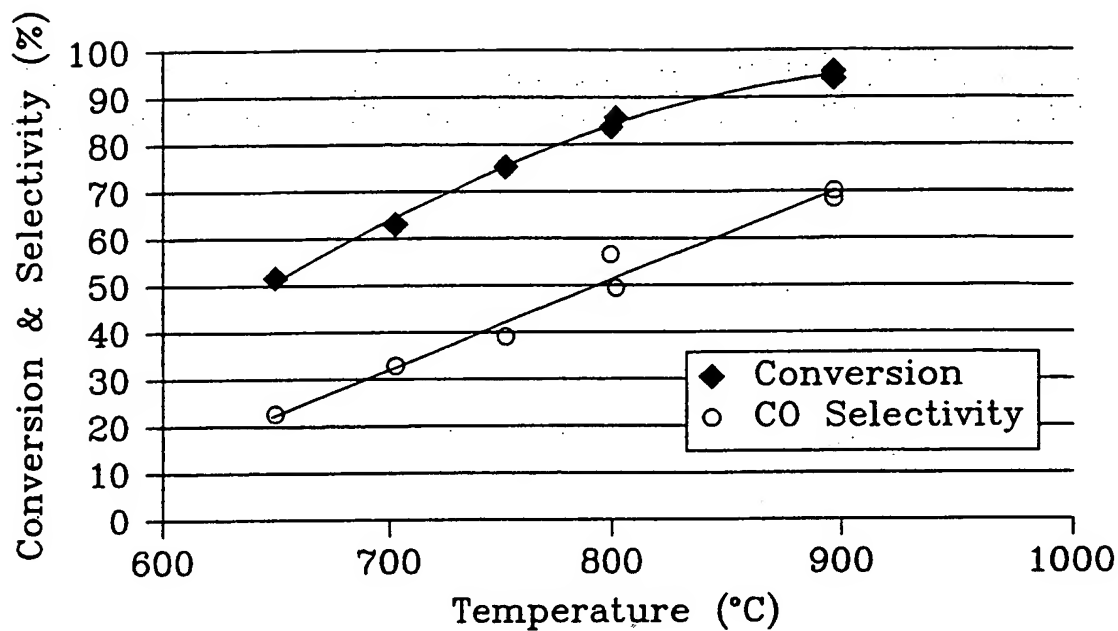
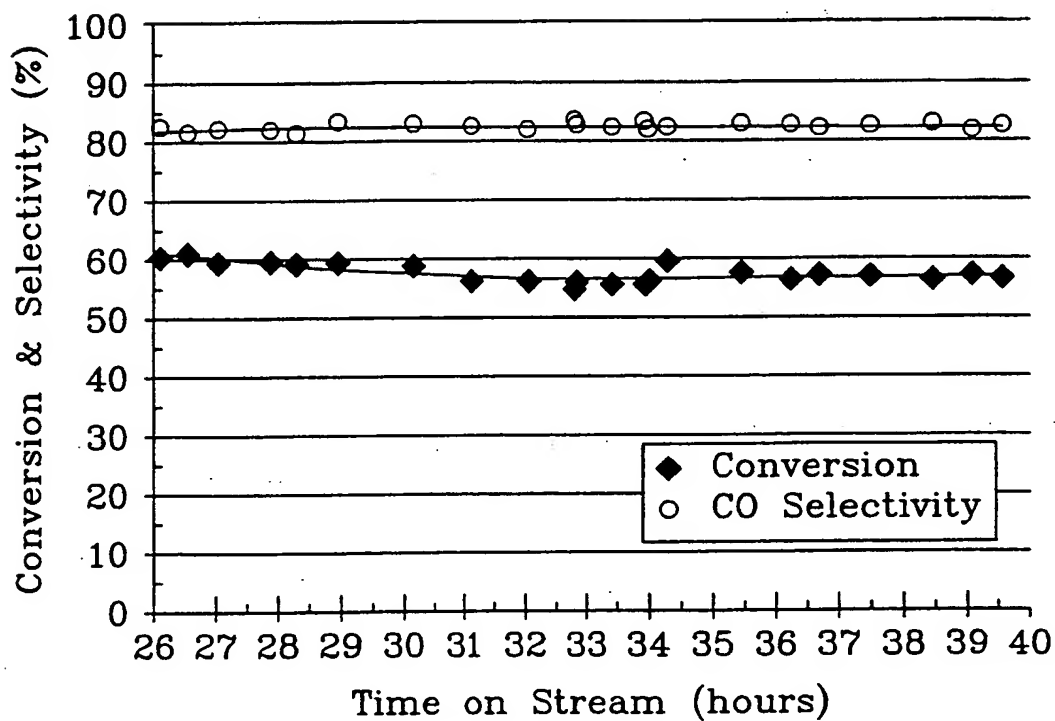
(c) a porous interfacial layer that is a spinel with a second pore surface area and a second pore size less than said first pore size, said porous interfacial layer having a thickness less than 4 mm placed upon said buffer layer;

(d) a steam reforming catalyst selected from the group consisting of rhodium, iridium, nickel, palladium, platinum, carbide of group IVb and combinations thereof placed upon said second pore surface area.

20

9. The catalyst structure as recited in claim 8, wherein said carbide is selected from the group of tungsten carbide, molybdenum carbide and combinations thereof.

25

*Fig. 1**Fig. 2*



# INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/US 00/22421

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 105 253 A (TOYO ENGINEERING CORP) 28 April 1972 (1972-04-28) page 8, line 18 -page 9, line 36 ---	1
A	US 4 088 608 A (ITO NOBUEI ET AL) 9 May 1978 (1978-05-09) claim 1; example 1 ---	1
A	GB 1 003 147 A (CHEMICAL CONSTRUCTION CORPORATION) 2 September 1965 (1965-09-02) page 2, line 95 -page 3, line 39 ---	1
A	US 5 679 614 A (BANGALA DENIS NGOY ET AL) 21 October 1997 (1997-10-21) column 9, line 60 -column 10, line 16; example 1 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

14 November 2000

Date of mailing of the international search report

21/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Clement, J-P

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 00/22421

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2105253 A	28-04-1972	AU 462426 B	26-06-1975
		AU 3310471 A	08-03-1973
		CA 949325 A	18-06-1974
		DE 2143608 A	09-03-1972
		NL 7112223 A, B,	07-03-1972
		SU 526281 A	25-08-1976
		US 3957681 A	18-05-1976
		US 4025457 A	24-05-1977
US 4088608 A	09-05-1978	JP 52074591 A	22-06-1977
		DE 2657126 A	30-06-1977
GB 1003147 A		NONE	
US 5679614 A	21-10-1997	CA 2114965 A	05-08-1995

Form PCT/ISA/210 (patent family annex) (July 1992)